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CHEMICAL SOCIETY.

Vol. 30 **No. 423.**

Thursday, January 22nd, 1914, at 8.30 p.m., Professor W. H. Perkin, LL.D., F.R.S., President, in the Chair.

The President referred to the loss sustained by the Society, through death, of:

	Elected.	Died.
William Popplewell Bloxam ..	Dec. 20th, 1883.	Dec. 26th, 1913.
John Gibson	June 16th, 1892.	Jan. 1st, 1914.

It was announced:

(*a*) That the Council desired to draw the attention of Fellows to the fact that the Faraday Society is prepared to consider the election to membership of a certain number of Fellows of the Chemical Society without the usual entrance fee.

(*b*) That Fellows may purchase the forthcoming Volume III. of the International Tables of Physical Constants and Numerical Data at the reduced prices of 19*s.* 3*d.* (unbound) or £1 2*s.* 3*d.* (bound). Application for this volume should be addressed to Dr. C. Marie, 9, Rue de Bagneux, Paris VI^{e}, before March 31st, 1914.

(*c*) That Volume II. of the Memorial Lectures delivered before the Chemical Society is now ready, and can be purchased from the Publishers or from the Assistant Secretary, price 6*s.* net.

The Council are considering the question of re-issuing Volume I. of the Memorial Lectures (now out of print), and it would be of

assistance to them if Fellows and others wishing to purchase it would send an intimation to this effect to the Assistant Secretary on the post-card which is issued with this number of the Proceedings.

Certificates were read for the first time in favour of Messrs.:

Sydney Edward Davenport, Fernbank, York Road, Windsor.
Charles George Fernie, B.Sc., Holmleigh, Northwood, Middlesex.
George Ingle Finch, 41, Ladbroke Road, W.
Reginald Furness, M.Sc., 90, Woodlands Road, Ansdell, Lytham.
Gopal Balkrishn Kolhatker, M.A., Ferguson College, Poona, India.
Frederic William Leighton, Lydiard Tregoze, Wootton Bassett, Swindon.
Rowland Ernest Oldroyd, 90, Park Road, Rochdale.
William Henry Pick, B.Sc., 141, Mare Street, Hackney, N.E.
Frederick Alfred Pickworth, 70, Highfield Road, Dartford.
Conly Hunter Riley, Anchorage, Clayton-le-Moors, Accrington.
Joseph de Carle Smith, B.Sc., Oak House, Newmarket Road, Norwich.
Horace Gilbert Stone, B.Sc., 24, High Street, High Wycombe.

A certificate has been authorised by the Council for presentation to ballot under Bye-law I (3) in favour of Mr. Lionel Cohen, Stock Department Laboratory, Casino, N.S.W.

Of the following papers, those marked * were read:

***1. "Crystals of organic compounds coloured blue by iodine." By George Barger and Walter William Starling.**

In a previous paper (Barger and Field, T., 1912, **101**, 1396) it was pointed out that the blue compounds formed from various organic substances and iodine may be either amorphous or crystalline; the former cases are typical examples of adsorption. The blue crystals may be regarded as solid solutions of iodine in the organic substance, in proportions not necessarily stoicheiometric. They only result when the crystal is formed in the presence of iodine, either from a solution containing iodine, or by sublimation in the presence of iodine (compare for analogous cases Bruni, *Feste Lösungen und Isomorphismus*, 1908, p. 95). Colourless crystals of the organic substance, when once formed, cannot be made to take up iodine. In most of the cases studied so far, the blue crystals have been obtained from solutions in mixtures of water with an organic solvent, but this need not be the case always; narceine,

for instance, when dissolved, together with iodine, in pyridine, gives rise to blue crystals on adding light petroleum. All the blue crystals examined so far are more or less strongly pleochroic; no connexion has been detected between the crystalline form and the capacity for yielding "mixed" crystals with iodine.

Discussion.

In reply to the President, Dr. Barger expressed the opinion that the additive compounds described might be analogous to oxonium compounds, but since they were also given by substances not containing a pyrone nucleus, they might possibly show greater analogy to the potassium additive compounds of ketones, described by Schlenk and Thal (*Ber.*, 1913, **46**, 2840). No analogous bromine compounds had been observed.

***2. "The mutual solubility of formic acid and benzene, and the system: benzene–formic acid–water." By Arthur James Ewins.**

Formic acid was found to be partly miscible with a number of organic liquids. The mutual solubility of formic acid with benzene was studied in detail.

The critical solution temperature (maximal) of these two liquids affords a very sensitive means of determining the purity of the components, and was therefore employed for this purpose. For the purification of formic acid, fractional distillation was employed, followed by careful fractional crystallisation, until the critical solution temperature with pure benzene remained constant (73·2°).

The acid so obtained melted at 8·39°, boiled at 100·47°/760 mm., and had D_4^{18} 1·2259. The acid showed very little supercooling on freezing, the actual figures in three determinations being 0·40°, 0·15°, and 0·35°.

Benzene was purified by fractional crystallisation and distillation from sodium. The melting point was found to be 5·57°. The ternary system benzene–formic acid–water was also studied.

***3. "The condensation of ethyl glutaconate." By Raymond Curtis and James Kenner.**

The condensation products isolated by Blaise (*Compt. rend.*, 1903, **136**, 639) and by von Pechmann (*Ber.*, 1904, **37**, 2113) from the action of sodium ethoxide on glutaconic ester were shown to be identical, and a probable constitution was assigned to them.

Certain discrepancies between the accounts given by the two investigators named were also examined.

α-Ethylglutaconic ester, after treatment with sodium ethoxide in the same manner as glutaconic ester, was recovered unchanged.

Discussion.

Prof. J. F. Thorpe stated that his experience with the behaviour of ethyl glutaconate on alkylation led him to think that the action of ethylene dibromide on this substance would most likely yield a derivative of *cyclo*pentane, and not the *cyclo*propane derivative suggested by Dr. Kenner. It would be of great interest to apply this reaction to the case of ethyl β-methylglutaconate, the two forms of which were sufficiently stable to withstand ordinary experimental conditions.

Dr. Kenner, in reply, pointed out that Fecht had proved one of the products of the condensation of ethyl glutaconate with ethylene dibromide to be a *cyclo*propane derivative by the identity of its reduction product with a synthetic acid of known constitution.

*4. "2-Hydrindamine."
By James Kenner and Annie Moore Mathews.

The preparation of 2-hydrindamine from ethyl hydrindene-2-carboxylate by Curtius's method was described, and the base was characterised by means of a number of derivatives.

*5. "An attempt to prepare organometallic derivatives of tungsten." By Eustace Ebenezer Turner.

It was shown that tungsten, in common with all elements situated in even series or in sub-group *A* of the periodic classification, cannot be converted into organo-metallic compounds by means of the Grignard reagent. The higher chlorides of tungsten are, instead, reduced, the chlorine removed decomposing the Grignard reagent to produce a mixed magnesium haloid salt and a hydrocarbon consisting of the two diaryl residues linked together, according to the general equation:

$$WCl_x + xRMgX = WCl_{x-2} + 2ClMgX + (x-2)RMgX + R{\cdot}R.$$

*6. "The absorption spectra of nitrated phenylhydrazones." By John Theodore Hewitt, Rhoda Marianne Johnson, and Frank George Pope.

The absorption spectra of the *p*-nitrophenylhydrazones of benzaldehyde and acetophenone have been measured. Addition of

alkali to the alcoholic solutions leads to salt-formation, accompanied by considerable change in the absorption spectra. The absorption of the two hydrazones mentioned is very similar to that of *p*-nitrobenzaldehydephenylhydrazone, although when the latter compound is acetylated, the absorption experiences a strong displacement towards the ultra-violet.

7. "Unstable compounds of cholesterol with barium methoxide." By Edgar Newbery.

Barium oxide in presence of excess of methyl alcohol forms an unstable solid compound with cholesterol, which is dissociated in organic solvents, such as ether, benzene, etc., to an extent depending on the temperature and also on the concentration of the excess of methyl alcohol present, a state of equilibrium being set up between the cholesterol in the solid and that in the liquid. This state of equilibrium is attained much more rapidly when the compound is being decomposed than when it is forming. The compound is readily decomposed by water, carbon dioxide, or acetic acid. Hexadecyl alcohol shows a similar behaviour to cholesterol.

A knowledge of the above reactions is of importance when attempting to extract cholesterol and cerebrones by Smith and Mair's method (*J. Path. Bact.*, 1910, **15**, 122).

8. "A study of the vapour pressure of nitrogen peroxide." By Alfred Charles Glyn Egerton.

Following some work on the vapour pressure of bromine, and in connexion with the measurement of small quantities of nitrogen peroxide, the vapour pressure of solid nitrogen peroxide has been investigated down to as low a temperature as $-100°$. The method employed in these measurements consisted in the saturation of a known volume of hydrogen, as it passed over the nitrogen peroxide, and the estimation of the amount of the latter carried over.

The measurements follow a certain curve which has a somewhat steeper slope than other measurements would appear to indicate, although these have not, so far, been carried below $-35°$. The vapour-pressure curve of nitrogen peroxide was discussed, and, with the aid of Nernst's vapour-pressure equation, approximate values of some of its chemical and physical constants were derived.

9. "Organic derivatives of silicon. Part XXI. The so-called siliconic acids." By Arthur James Meads and Frederic Stanley Kipping.

Many compounds supposed to have the structure R·SiO·OH and to represent the silicon analogues of the carboxylic acids have been described in the literature. The first case was that of silicopropionic acid, $EtSiO_2H$ (Friedel and Ladenburg); shortly afterwards silicoacetic acid, $Me{\cdot}SiO_2H$, silicobenzoic acid, $Ph{\cdot}SiO_2H$, and silicotoluic acid, $C_6H_4Me{\cdot}SiO_2H$, were described by Ladenburg (*Annalen*, 1875, **179**, 143). In more recent times many other aliphatic and aromatic siliconic acids have been prepared by Khotinsky and Seregenkoff (*Ber.*, 1908, **41**, 2946), and by Melzer (*Ber.*, 1908, **41**, 3390).

Now the results of the study of the diarylsilicanediols, $R_2Si(OH)_2$ (Kipping, T., 1912, **101**, 2108, 2125; Robison and Kipping, *ibid.*, 2142, 2156), seemed to indicate that compounds of the type $RSi(OH)_3$ would not pass into siliconic acids, $R{\cdot}SiO_2H$, by loss of the elements of water, but would give rise to a series of condensation products, probably analogous to those of the diarylsilicanediols. An exhaustive examination of the so-called silicobenzoic acid has gone far to establish this view: the product of the hydrolysis of phenylsilicon trichloride is not one compound of the composition $C_6H_5{\cdot}SiO_2H$, but a complex mixture of condensation products, primarily derived from the trihydroxy-derivative, $C_6H_5{\cdot}Si(OH)_3$. It is very probable, therefore, that all the so-called siliconic acids are merely mixtures; the experiments are being continued in order to test this inference.

10. "The reactions of *iso*amarine." By Henry Lloyd Snape.

*iso*Amarine and methyl iodide react at the ordinary temperature, when benzene is employed as a solvent, with the production of the *methiodide*, $(C_{21}H_{18}N_2)_2,CH_3I$, which, on crystallisation from benzene, melts at 135°.

By the action of acetyl chloride on a solution of *iso*amarine in ethyl acetate or chloroform and heating the product with absolute alcohol, a crystalline substance, melting at 235—236°, was obtained, which proved to be an isomeride of the compound called "diacetylamarine" by Bahrmann, but shown by Japp and Moir (T., 1900, **77**, 636) to be acetylbenzoyldiphenylethylenediamine, $C_{23}H_{22}O_2N_2$, which melts at 316°. The six-sided plates mentioned in a former paper (T., 1900, **77**, 780) as having been obtained in small quantity as the result of the action of acetyl chloride on *iso*amarine followed by treatment with alcohol, proved to be *iso*amarine hydrochloride.

When *iso*amarine, dissolved in a very small quantity of glacial acetic acid, was treated with fuming nitric acid, a *mononitro*-derivative was obtained, which melted at 82—85°. Fuming nitric acid at 60° acted on *iso*amarine, forming a *dinitro*-derivative, which melted at 175—176°.

The values previously published for the rotation of *d*- and *l-iso*amarine and of the corresponding tartrates have been corrected.

Sulphates of *d*- and *l-iso*amarine were described. The former has the formula $(C_{21}H_{18}N_2)_2,H_2SO_4$, melts at 266—267°, and its rotatory power, $[\alpha]_D$, is +151·1° to +155·7°. The corresponding particulars with respect to the lævo-salt are $(C_{21}H_{18}N_2)_2,H_2SO_4,\frac{1}{2}H_2O$, 280—285°, and −144·1°. On addition of nitrosyl sulphate to *d-iso*amarine sulphate, a white, crystalline substance is precipitated which has the composition $(C_{21}H_{18}N_2)_2,H(NO)SO_4,\frac{1}{2}H_2O$.

11. **"The constituents of Solanum angustifolium: isolation of a new gluco-alkaloid, solangustine." By Frank Tutin and Hubert William Bentley Clewer.**

The material employed in this investigation consisted of the leaves, twigs, and flowers of *Solanum angustifolium*, Ruiz et Pavon.

For the purpose of a complete examination, 30·92 kilograms of the dried and ground material were completely extracted with hot alcohol, and the resulting extract distilled with steam.

From the portion of the extract which was soluble in water, there were isolated the following substances: (i) quercetin; (ii) rutin; (iii) *l*-asparagine; (iv) a new gluco-alkaloid, *solangustine*, $C_{33}H_{53}O_7N,H_2O$. The aqueous liquid also contained small amounts of an amorphous alkaloid and a considerable quantity of sugar, together with amorphous, viscid products which, on hydrolysis, yielded quercetin and 3:4-dihydroxycinnamic acid.

The portion of the extract which was insoluble in water yielded the following definite substances: (i) triacontane; (ii) a phytosterol, $C_{27}H_{46}O$; (iii) a phytosterolin (phytosterol glucoside), $C_{33}H_{56}O_6$; (iv) palmitic, stearic, cluytinic, and cerotic acids, together with a mixture of linolic and linolenic acids.

The *hydrochloride*, *nitrate*, and *sulphate* of solangustine are insoluble in water and most organic solvents. The last-mentioned salt forms colourless needles, and has the formula $(C_{33}H_{53}O_7N)_2H_2SO_4,3H_2O$.

On hydrolysis with dilute acid, solangustine yields *solangustidine*, $C_{27}H_{43}O_2N$, and dextrose:

$$C_{33}H_{53}O_7N + H_2O = C_{27}H_{43}O_2N + C_6H_{12}O_6.$$

Solangustidine is amorphous, but a crystalline *hydrochloride*,

hydrobromide, nitrate, sulphate, picrate, and *acetyl* derivative have been prepared from it.

The entire alcoholic extract of the plant, the new gluco-alkaloid, solangustine, and the amorphous, alkaloidal material were separately administered to a dog, but produced no appreciable physiological effect.

12. "Studies of the constitution of soap solutions: electrical conductivity of potassium salts of fatty acids." By Hugh Mills Bunbury and Herbert Ernest Martin.

The conductivities of the potassium salts (soft soaps) of the saturated fatty acids of even number of carbon atoms from the stearate to the acetate have been measured at 90° by the somewhat laborious method previously described by McBain and Taylor.

The conductivities of the potassium soaps are higher than those of the corresponding sodium soaps, but there is a general resemblance between the form and position of corresponding curves. Closer comparison shows an even greater tendency towards abnormality on the part of the potassium salts; this is not due to the potassium ion as such, for well-developed maxima and minima in the conductivity curves are exhibited from the stearate as far down as the laurate (C_{12}).

The appearance, washing power, density, and conductivity curve of potassium hexoate (C_6) distinctly mark the beginning of that deviation from the behaviour of the acetate, which rapidly and regularly increases through the other members of the homologous series until it attains the typical character of the higher soaps.

In all cases where it is directly visible, the depression in the conductivity curve occurs in the same region of concentration, independent of the nature of the acid or alkali taken. Further investigation may, however, show that the real abnormality is shifted in the case of the lowest homologues to regions of higher concentration.

13. "The system ethyl ether–water–potassium iodide–mercuric iodide. Part I. The underlying three-component systems." By Alfred Charles Dunningham.

The System: Potassium iodide–mercuric iodide–water.—This system has been studied at 20° and 30°. In both cases the following phases are stable in equilibrium with solution: KI, $KHgI_3$, $KHgI_3,H_2O$, HgI_2.

The System: Potassium iodide–water–ethyl ether.—Ether and

water are only miscible to a small extent, and this is not materially increased by the addition of potassium iodide. Consequently it is possible to obtain: (1) A small range of homogeneous aqueous solutions in equilibrium with potassium iodide, (2) a small range of homogeneous ethereal solutions in equilibrium with potassium iodide, (3) one pair of invariant aqueous and ethereal solutions in equilibrium with one another and with potassium iodide, and (4) a wide range of conjugate aqueous and ethereal solutions in equilibrium with one another.

The System: Potassium iodide–mercuric iodide–ethyl ether.—The following phases are stable in equilibrium with solution: KI–$KHgI_3$–HgI_2. Under certain conditions a heavy liquid layer separates, rich in dissolved salts, and an equilibrium diagram has been constructed in which the saturation curves of potassium mercuri-iodide and mercuric iodide are cut by a binodal curve, so that each is divided into two portions, separated by a region in which all mixtures exist as two liquid layers.

The System: Mercuric iodide–water–ethyl ether.—Mercuric iodide is almost insoluble in water and ether and all mixtures of these two components. The equilibrium is of the same type as that in the system: potassium iodide–water–ethyl ether.

14. "The inversion of sucrose by acids in water–alcohol solutions." By George Joseph Burrows.

The rate of inversion of sucrose by acids in water–ethyl alcohol mixtures decreases with increasing concentration of alcohol up to 45—50 per cent., and then increases. The catalysis in such a series of solvents is therefore not proportional merely to the concentration of hydrogen ions. The catalytic activity of an acid is affected by the viscosity of the solution, and the influence of the latter is probably the same as in conductivity. If, therefore, the rates of inversion are divided by the conductivities of the acid in the different solvents, the numbers so obtained represent the relative catalytic activities of the acid. In this way it was found that the replacement of water by alcohol increases the catalytic activity of hydrochloric acid.

In the inversion of sucrose by acids, therefore, the addition of water may be regarded as decreasing the catalytic activity of the hydrogen ions. This agrees with results obtained by other authors for the anti-catalytic effect of the addition of water in esterification and similar catalytic reactions in alcohol.

15. "The volatile oil of Cymbopogon coloratus from Fiji." By Ernest Goulding and John Campbell Earl.

The essential oils derived from certain species of Cymbopogon are well known in commerce as "lemon-grass" and "citronella" oils. The former are derived mainly from *Cymbopogon flexuosus*, Stapf, and *C. citratus*, Stapf, and the latter from *C. Nardus*, Rendle. The chief constituent of the lemon-grass oils is citral, the proportion of which is commonly between 70 and 80 per cent. The citronella oils, on the other hand, are characterised by the presence of considerable quantities of citronellaldehyde and geraniol, but contain very little or no citral.

In the course of a study of the various grass oils at the Imperial Institute, three oils have been encountered which have not hitherto been described, and exhibit characters very different from those of either the lemon-grass or citronella oils. One of these is furnished by the leaves of *Cymbopogon coloratus*, Stapf, and contains considerable quantities of citral and geraniol, but no citronellaldehyde.

In 1907, seeds of a lemon-grass were forwarded to Fiji from India, and the plant, since identified as *Cymbopogon coloratus*, Stapf, has been grown at Nasinu Experiment Station. It has been found by Knowles (*Bull. No.* 6, *Dept. Agric. Fiji*) that the fresh leaves of this grass, when distilled with steam, yield about 0·35 per cent. of oil. Samples of oil distilled in Fiji were forwarded to the Imperial Institute in 1908 and 1909, and were subjected to a preliminary investigation (*Bull. Imp. Inst.*, 1912, **10**, 27). Subsequently the oil was examined by Umney (*Perfumery and Essential Oil Record*, Dec., 1912, 317), who found it to contain 35 per cent. of citral and 30 per cent. of geraniol. A further sample of the oil has been received recently from Fiji, and has been submitted to examination, with the following results.

The oil had D_{15}^{15} 0·912 and $[\alpha]_D$ at 24°, −10·31°, and contained 23 per cent. of geraniol (estimated by the phthalic anhydride method). It was shaken successively with sodium carbonate, sodium hydrogen sulphite, and sodium hydroxide, and the residual oil was afterwards submitted to fractional distillation. The sodium carbonate solution extracted 0·75 per cent. of the oil, consisting chiefly of acetic acid. The sodium hydrogen sulphite removed 34 per cent. of aldehydes, but some of the aldehyde remained in the residual oil (see below). The aldehydic constituents had a pleasant, lemon-like odour, and consisted almost entirely of citral. The treatment with sodium hydroxide extracted 0·75 per cent. of phenolic substances, from which a small quantity of a white, tasteless, and odourless solid (m. p. 142°, decomp.) was isolated;

the remainder consisted of a dark brown liquid with an odour recalling that of cloves, but the quantity was too small to admit of identification.

The residual oil still possessed a lemon-like odour, and an aldehyde estimation made by the sulphite method showed an absorption of 11 per cent. It furnished the following constants: D_{15}^{15} 0·915; α_D^{20} −12°29′ (in 1-dcm. tube); ester value 42 (corresponding with 14·7 per cent. of geranyl acetate and equivalent to 9·5 per cent. in the original oil); saponification value after acetylation, 183 (corresponding with 43·4 per cent. of alcohols, calculated as $C_{10}H_{18}O$). On distillation under 10—12 mm. pressure, the following fractions were obtained:

Fraction.	Temperature.	Quantity, per cent.	D_{15}^{15}	Optical rotation, in 1-dcm tube.
A	up to 80°	8·3	0·858	−52°22′
B	80—105	2·7	0·868	38 35
C	105—120	27·1	0·902	12 55
D	120—130	25·5	0·912	6 4
E	130—150	13·7	0·937	4 32
F	residue and loss	22·7	—	—

Fraction A consisted largely of terpenes. A further quantity of terpenes was obtained by distilling some of the original oil on the water-bath under 15—20 mm. pressure. By this means a fraction amounting to 7·4 per cent. of the original oil was obtained, which after repeated treatment with sodium and redistillation had D_{15}^{15} 0·854, α_D^{20} −62°39′ (in 1-dcm. tube), and b. p. 168—173°/760 mm. The terpenes absorbed bromine to an extent corresponding with about three atoms per mol. $C_{10}H_{16}$, but the product could not be obtained in a crystalline state. It is probable that the terpenes were a mixture of *l*-limonene with one or more other terpenes, but the quantity of oil available was not sufficient to enable them to be identified.

Fraction B appeared to contain the constituents of A and C, and was not examined in detail.

Fraction C consisted chiefly of geraniol.

Fraction D contained more than 20 per cent. of esters. After hydrolysis, it yielded a homogeneous, crystalline diphenylurethane of geraniol (m. p. 82°). The readiness with which this derivative crystallised indicated the absence of citronelloldiphenylurethane.

Fraction E was readily soluble in less than three volumes of 70 per cent. alcohol (indicating the absence of sesquiterpenes), and furnished geranioldiphenylurethane (m. p. 82°).

The residue F was dark brown and viscous. When submitted to distillation in steam, about one-fourth of it distilled over; the remainder probably consisted of resinous, non-volatile, polymerisa-

tion products formed during the distillation and fractionation of the oil.

The results of this investigation indicate that the oil of *Cymbopogon coloratus* has the following approximate composition:

Terpenes	7·5 per cent.
Aldehydes, chiefly or entirely citral	40 ,,
Geraniol	23 ,,
Esters, chiefly geranyl acetate	10 ,,
Acetic acid	0·75 ,,
Phenols	0·75 ,,
Substances not identified	18 ,,

16. "The hydrolysis of mixed secondary amides by alkalis." By Arthur Walsh Titherley and Leonard Stubbs.

A mixed secondary amide, $R{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}R'$, under the influence of alkali, may conceivably suffer hydrolysis in two possible ways: (1) giving $R{\cdot}CO_2H$ and $R'{\cdot}CO{\cdot}NH_2$, or (2) giving $R{\cdot}CO{\cdot}NH_2$ and $R'{\cdot}CO_2H$. Direction (1) is followed exclusively when R′ is an aromatic radicle and R is methyl, and this is attributed by the authors to steric influence. The mechanism of hydrolysis is probably one in which water-addition first takes place at the double link (C:N) of the tautomeric form of the secondary amide, yielding $R{\cdot}C(OH)_2{\cdot}NH{\cdot}CO{\cdot}R'$, which then decomposes into the acid $R{\cdot}CO_2H$ and amide $R'{\cdot}CO{\cdot}NH_2$. Accordingly, in the equilibrium:

$$\underset{\text{(I.)}}{R{\cdot}C(ONa){:}N{\cdot}CO{\cdot}R'} \rightleftharpoons \underset{\text{(II.)}}{R{\cdot}CO{\cdot}N{:}C(ONa){\cdot}R'}$$

the rate of hydrolysis of I is very much greater than that of II, and owing to continual disturbance of the equilibrium it is the only form the hydrolysis of which can be detected. Whilst the hydrolysis of diacetamide, acetylcarbamide, and acetobenzamide in the cold is complete within forty minutes, that of purely aromatic secondary amides under the same conditions requires about fifteen hours. The influence of spacial protection on the course of the hydrolysis is illustrated by the fact that benzo-*o*-toluamide, $Bz{\cdot}NH{\cdot}CO{\cdot}C_6H_4{\cdot}CH_3$, yields benzoic acid and *o*-toluamide exclusively, whilst benzo-*p*-toluamide decomposes in both possible ways, yielding a mixture of benzoic and *p*-toluic acids, together with benzamide and *p*-toluamide. Although steric influence is potent in directing the course of hydrolysis of a mixed secondary amide, evidence is available that the affinity for water of the double link (C:N) is also a factor. In the hydrolysis of acetylcarbamide, which yields acetic acid and carbamide almost quantitatively, it is probable that the form $CH_3{\cdot}C(ONa){:}N{\cdot}CO{\cdot}NH_2$ only is involved. The two benzotoluamides above were obtained best by the condensation

of the corresponding phenyl toluates and benzamidine, and subsequent hydrolysis of the resulting toluoylbenzamidines,

$$NH{:}CPh{\cdot}NH{\cdot}CO{\cdot}C_6H_4Me.$$

17. The miscibility of azobenzene and azoxybenzene in the solid state and the supposed existence of a stereoisomeride of azobenzene." By Harold Hartley and John McArthur Stuart.

An examination of the freezing-point and melting-point curves of mixtures of azobenzene and azoxybenzene has shown that these substances form two series of mixed crystals with an eutectic temperature of 24·5°. The two mixed crystals deposited at this temperature contain respectively 45 per cent. and 90 per cent. of azoxybenzene molecules. The latter crystals are probably identical with the substance obtained by C. V. and R. A. Gortner (*J. Amer. Chem. Soc.*, 1910, **22**, 1294) as a by-product in the preparation of azobenzene by the distillation of azoxybenzene with iron filings, and thought by them to be a stereoisomeride of azobenzene.

18. "The influence of colloids and fine suspensions on the solubility of gases in water. Part IV. Solubility of nitrous oxide at pressures lower than atmospheric." By Alexander Findlay and Owen Rhys Howell.

In continuance of previous work (T., 1910, **97**, 536), the solubility of nitrous oxide in water in the presence of ferric hydroxide, dextrin, starch, gelatin, egg-albumin, silicic acid, finely divided silica, and finely divided charcoal, has been determined at pressures lower than atmospheric. The values obtained fit in well with those previously obtained at higher pressures, and the general type of solubility curve obtained is similar to that found in the case of carbon dioxide (T., 1910, **97**, 536; 1913, **103**, 636); that is to say, the solubility curves show a more or less pronounced minimum.

19. "The action of aldehydes on the Grignard reagent." By Joseph Marshall.

It has been found that the addition of two molecular proportions of benzaldehyde to one molecular proportion of magnesium methyl iodide results in the formation of *α*-methyldeoxybenzoin,

$$C_6H_5{\cdot}CH(CH_3){\cdot}CO{\cdot}C_6H_5.$$

The course of this reaction is indicated by the equations:

$$C_6H_5{\cdot}CH(CH_3){\cdot}OMgI + C_6H_5{\cdot}CHO = C_6H_5{\cdot}CH(CH_3){\cdot}C(C_6H_5)(OH){\cdot}OMgI.$$

$$C_6H_5{\cdot}CH(CH_3){\cdot}C(C_6H_5)(OH){\cdot}OMgI + H_2O = C_6H_5{\cdot}CH(CH_3){\cdot}CO{\cdot}C_6H_5 + H_2O + Mg(OH)I.$$

A similar result was obtained when benzaldehyde was allowed to react with magnesium dimethylcarbinyl iodide, in which case phenyl *iso*propyl ketone was isolated. When, however, two molecules of benzaldehyde were caused to react with one molecule of magnesium phenyl bromide, the products of the reaction were benzyl alcohol and benzophenone, instead of phenyldeoxybenzoin (triphenylvinyl alcohol), as was expected. This result may be explained by assuming that the triphenylvinyl alcohol is hydrolysed under the conditions of the experiment as follows:

$$(C_6H_5)_2C{:}C(OH)\cdot C_6H_5 + H_2O = (C_6H_5)_2CO + C_6H_5\cdot CH_2\cdot OH.$$

An analogous equation would explain the production of acetophenone when acetaldehyde is allowed to react with magnesium phenylmethylcarbinyl bromide.

An attempt was made to obtain phenylmethylacetaldehyde by allowing trioxymethylene to react with magnesium phenylmethylcarbinyl iodide, but the product of this reaction was phenylethyl iodide. Similar products were obtained when ethyl formate reacted with Grignard reagents, instead of the substituted acetic esters which were expected in these reactions.

20. "The use of sulphuryl chloride in the alkylation of phenols." By Wilhelmina Rebecca Smyth.

In view of the poisonous character of methyl sulphate, experiments have been carried out to ascertain whether it would be possible to use methyl alcohol and sulphuryl chloride in place of methyl sulphate as a methylating agent, and also whether other alcohols than methyl alcohol would react with phenols in the presence of sulphuryl chloride. The sulphuryl chloride was added to a slight excess of the alcohol, and when action was at an end the phenol was introduced. The mixture was allowed to remain for some time, and then treated gradually with a slight excess of alkali hydroxide. The ether formed was either extracted from the alkaline solution or removed by distillation in steam. In some cases before introducing the sulphuryl chloride the alcohol was treated with the calculated amount of metallic sodium, but this addition was not found to have any appreciable influence on the result. In other cases the sulphuryl chloride was cooled in a freezing mixture, and the alcohol slowly added, but here also the yields were not affected to any great extent.

The phenols treated in this way were phenol, catechol, carvacrol, and β-naphthol, the alcohols used being methyl and ethyl alcohol, and, in the case of the two last compounds, propyl alcohol. In all these cases alkylation occurs under the conditions just described,

but, except in the case of β-naphthol, the ethers are only formed in small amounts. β-Naphthol yields about half the calculated amounts of the methyl, ethyl, and propyl ethers. Phenol gave from 15 to 25 per cent. of anisole and phenetole, and catechol about 20 per cent. of guaiacol, but no veratrole. Carvacrol gave only traces of the methyl, ethyl, and propyl ethers. In most cases practically the whole of the unchanged phenol could be recovered from the alkaline solution.

Attempts to alkylate amino-compounds in a similar manner were not successful.

21. "The colours produced on mixing the alkyl nitrites with substances containing centres of residual affinity." By Ernest Magowan Harper and Alexander Killen Macbeth.

In view of the fact that many colour reactions have recently been obtained with the organic nitro-compounds, it appeared of interest to the authors to examine the alkyl nitrites. It was shown that these give colours with amino-compounds, ethylenic hydrocarbons and substances containing bivalent sulphur. These colours are similar to those obtained with tetranitromethane when treated with the same substances. It is thought probable that the colour is due to an intermediate additive compound, the true final additive compound being colourless. Parallel to this is the Vorländer hypothesis, which deals with such cases to account for the two products when an acid reacts with an αβ-unsaturated ketone.

The final additive products of the nitrites and the primary, secondary, and tertiary amines have been isolated by Rây and Datta, Rây and Rakshit, and by Neogi, and the preparation of the corresponding compounds in case of the bivalent sulphur substances is being undertaken by the authors.

22. "The progressive bromination of toluene" By Julius Berend Cohen and Pavitra Kumar Dutt.

Cohen and Dakin (T., 1901, **79**, 1111) studied the progressive chlorination of toluene through successive stages from the hydrocarbon to the tetrachloro-derivatives. The results described by A. K. Miller (T., 1892, **61**, 1023) on the bromination of *o*- and *p*-bromotoluene present certain differences in the quantity and character of the products when compared with those obtained by chlorination of the corresponding chlorotoluenes. The authors have therefore submitted the subject to a careful investigation, in which they have determined the character of all the bromine deriv-

atives obtained by brominating the hydrocarbon and its mono- and di-bromo-derivatives.

The results of chlorination and bromination are given side by side in the following table for comparison, the principal product being placed first in each case, those occurring in smaller quantity standing next in order, whilst a trace is indicated by brackets.

Substance taken.		Bromination products.	Chlorination products.
	Toluene	ortho, para, (meta)	ortho, para
Mono-halogen compounds	Ortho	2 : 5, 2 : 4	2 : 4, 2 : 3, 2 : 6, (2 : 5)
	Meta	2 : 5, 3 : 4, (3 : 5)	2 : 5, 3 : 4
	Para	2 : 4, 3 : 4	2 : 4, 3 : 4
Dihalogen compounds	2 : 3	2 : 3 : 6, 2 : 3 : 5	2 : 3 : 4
	2 : 4	2 : 4 : 5, (2 : 4 : 6)	2 : 4 : 5, 2 : 3 : 4, (2 : 4 : 6)
	2 : 5	2 : 4 : 5, (2 : 3 : 6)	2 : 3 : 6, 2 : 4 : 5
	2 : 6	2 : 3 : 6	2 : 3 : 6
	3 : 4	2 : 4 : 5, (3 : 4 : 5)	2 : 4 : 5
	3 : 5	2 : 3 : 5	2 : 3 : 5

Attention was directed to the difference in orienting effect produced by chlorination and bromination of the ortho-halogen derivatives, which is most marked in the case of the *o*-bromotoluene and in that of the 2 : 3- and 2 : 5-dihalogen derivatives.

23. "The absorption spectra of some mercury compounds." By Cecil Reginald Crymble.

It has been shown that groups attached to the mercury atom increase its absorptive power in the following order: CN, Cl, $C_2H_3O_2$, $C_3H_5O_2$, Hg, Br, NO_2, I; and that the absorption of the molecule depends on an interaction between the mercury atom and the attached groups.

Entrance of the mercury atom into complex haloid salts is accompanied by an increase in absorptive power. It is possible to determine the nature of the complex formed, and to follow its progressive dissociation on dilution. The complex $MHgX_3$ is formed quantitatively at decimolecular concentrations in alcohol. There is no spectroscopic evidence of the formation of any higher complex, such as M_2HgX_4, in either alcohol or water.

The change in the properties of the mercury atom on passing from the dihaloid salt to the dialkyl compound has been compared with the corresponding change in the absorption spectra of these compounds.

24. "A new phosphoric ester obtained by the aid of yeast-juice." (Preliminary note.) By Arthur Harden and Robert Robison.

In the preparation of hexosediphosphoric acid from lævulose and disodium hydrogen phosphate a second phosphoric acid derivative

is also obtained. This is found in the filtrate after the separation of the diphosphate by treatment with lead acetate, and is precipitated on the addition of a solution of basic lead acetate. A portion of the new compound is also precipitated along with the lead hexosediphosphate, from which it can be separated by decomposing the salt with hydrogen sulphide, reprecipitating with lead acetate, and repeating these operations several times.

By decomposing the basic lead salt with hydrogen sulphide an aqueous solution of the acid itself may be prepared. It gives Seliwanoff's reaction, reduces Fehling's solution, and yields an osazone. It is strongly dextrorotatory, the specific rotation being very much higher than that of hexosediphosphoric acid. When the solution is boiled phosphoric acid is liberated and the rotatory power falls, whilst the reducing power is slightly increased.

The barium salt was obtained by neutralising the solution of the acid with baryta, filtering, and adding an equal volume of alcohol, whereupon the salt was precipitated as a white, amorphous solid. It is readily soluble in both hot and cold water, differing in this respect markedly from barium hexosediphosphate. Various methods of purification have been employed, but the salt has not yet been obtained entirely free from nitrogenous impurities. The results of analyses, however, approximate fairly closely to those required for the barium salt of a hexosemonophosphoric acid, $C_6H_{11}O_6 \cdot PO_3Ba$.

A similar compound is also obtained when dextrose is substituted for lævulose, but it has not yet been ascertained whether these two compounds are or are not identical. The investigation is being continued, and the relations of this substance to hexosediphosphoric acid and to the process of alcoholic fermentation are being studied.

ADDITIONS TO THE LIBRARY

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Dumas, ***Jean Baptiste,*** **Stas,** ***Jean Servais,*** **and Boussingault,** ***Jean Baptiste Joseph Dieudonné.*** **L'air, l'acide carbonique, et l'eau. (Les Classiques de la Science, Vol. I.) Paris 1913. pp. xii + 104, ill. 1 Fr. 30. (*Recd.* 16/12/13.) From the Publisher: Armand Colin**

Foucault, ***Léon.*** **Mesure de la vitesse de la lumiere. Étude optique des surfaces. (Les Classiques de la Science, Vol. II.) Paris 1913. pp. xii + 122. ill. 1 Fr. 30. (*Recd.* 16/12/13.)**

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Gay-Lussac, *Louis Joseph,* **Avogadro,** *Amedeo,* **Ampère,** *André Marie,* **Dumas,** *Jean Baptiste,* **Gaudin,** *Antoine,* and **Gerhardt,** *Charles Frédéric.* Molécules, atomes, et notations chimiques. (Les Classiques de la Science, Vol. IV.) Paris 1913. pp. xiv + 116. ill. 1 Fr. 30. (*Recd.* 16/12/13.) From the Publisher: Armand Colin.

Redwood, *Sir Boverton.* Petroleum: A treatise on the geographical distribution and geological occurrence of petroleum and natural gas; the physical and chemical properties, production, and refining of petroleum and ozokerite; the characters and uses, testing, transport, and storage of petroleum products; and the legislative enactments relating thereto; together with a description of the shale oil and allied industries; and a full bibliography. 3rd edition. 3 vols. London 1913. pp. xxxii + 367, 417, 382. ill. 50*s.* net. (*Recd.* 9/12/13.) From the Author.

Thénard, *Louis Jacques,* **Schönbein,** *Christian Friedrich,* **Marignac,** *Jean Charles Galissard de,* **Soret,** *Jacques Louis,* **Troost,** *Louis Joseph,* **Hautefeuille,** *Paul,* and **Chappuis,** *James.* Eau oxygénée, et ozone. (Les Classiques de la Science, Vol. III.) Paris 1913. pp. xii + 111. ill. 1 Fr. 20. (*Recd.* 16/12/13.)

From the Publisher: Armand Colin.

II. *By Purchase.*

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Georgievics, *George von.* Lehrbuch der chemischen Technologie der Gespinstfasern. I. Lehrbuch der Farbenchemie. 4th edition, edited by *Eugène* **Grandmougin.** Leipzig 1913. pp. xiv + 570. M. 15.—. (*Recd.* 10/12/13.)

Partington, *James Riddick.* A text-book of thermodynamics. With special reference to chemistry. London 1913. pp. x + 544. 14*s.* net. (*Recd.* 10/12/13.)

Sabatier, *Paul.* La catalyse en chimie organique. Paris 1913. pp. xiv + 255. 10 Fr. (*Recd.* 16/12/13.)

Wilson, *H. Maclean,* and **Calvert,** *H. T.* Trade waste waters: their nature and disposal. London 1913. pp. xii + 340. ill. 18*s.* net. (*Recd.* 10/12/13.)

At the next Ordinary Scientific Meeting, on Thursday, February, 5th, 1914, at 8.30 p.m., the following papers will be communicated:

"The absorption spectra of the vapours and solutions of various substances containing two benzene nuclei." By J. E. Purvis.

"The oxidation of some benzyl compounds of sulphur. Part II. Benzyl tetrasulphoxide." By J. A. Smythe.

"The reaction between iodine and aliphatic aldehydes." By H. M. Dawson and J. Marshall.

"The erosion of lead." By J. F. Liverseege and A. W. Knapp.

"Acylation as influenced by steric hindrance: the action of acid anhydrides on 3: 5-dinitro-*p*-aminophenol." By R. Meldola and W. F. Hollely.

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